Biomethane Standards Discussion

April 25, 2013

Sacramento, CA

Discussion Topics

- Biogas source-specific constituents of concern
- OEHHA health protective levels
- Proposed risk management approach
  - Monitoring & testing requirements
  - Reporting & recordkeeping requirements
- Open discussion and wrap-up

Biogas Source Specific Constituents of Concern

Constituent	Landfill	POTW	Dairy
Antimony	X		
Arsenic	X		
Copper	X		
p-Dichlorobenzene	X	X	
Ethylbenzene	X	X	X
Hydrogen Sulfide	X	X	X
Lead	X		
Methacrolein	X		
n-Nitroso-di-n-propylamine	X		X
Mercaptans (alkyl thiols)	X	X	X
Toluene	X	X	X
Vinyl Chloride	X	X	

Exclusion of Benzene from CoCs

Benzene Average and High Values in Natural Gas and Landfill Biogas Samples (ppmv)				
	Pipeline Quality Natural Gas	Landfills		
		Biogas	Biogas AP-42	Bio-methane
Mean *	13.4	1.7	2.4	< 1
Highest Site Value	38.6	3	22	< 1
Sites Sampled	8	6	41	7

* Mean of site means for landfills, and mean of 8 different sources of natural gas.

OEHHA Proposed Health Protective Levels for Constituents of Concern

Constituent	OEHHA Health Protective Limit (mg/m^3)	OEHHA Health Protective Limit (ppm)
Vinyl Chloride*	0.84	0.33
Dichlorobenzenes (as p-Dichlorobenzene)*	5.7	0.95
n-Nitroso-di-n-propylamine*	0.033	0.0062
Ethylbenzene*	26	6.0
Arsenic*	0.019	0.0062
Hydrogen Sulfide**	30	22
Antimony**	0.60	0.12
Methacrolein**	1.10	0.38
Toluene**	900	240
Alkyl thiols (mercaptans)**	N/A	12
Copper**	0.060	0.023
Lead**	0.075	0.0089

Residential risk at one chance per million or Chronic HQ at 0.1
*Potential Cancer risk
**Chronic Non-cancer risk

Risk Management Approach

- Relies on ARB and OEHHA's exposure modeling and risk analysis
- Similar to approach in ARB's *Risk Management Guidelines for New and Modified Sources of Toxic Air Pollutants*
  - Integrate risk levels into risk management decisions
  - Identify trigger levels and lower and upper action levels
  - Consider cancer and non-cancer risks
  - Ensure potential health risks are avoided

Proposed Cancer and Non-cancer Risk Levels and Actions

Risk Management Approach	Potential Cancer Risk (chances/10^6)	Non-cancer total hazard index (HI)	Action/Monitoring Frequency
Below Trigger Level	<1[a]	<0.1[a]	Annual Testing
Trigger Level (OEHHA Health Protective Level)	≥1[a]	≥0.1[a]	Quarterly Testing
Lower Action Level (LAL)	≥10[b]	≥1[b]	Quarterly Testing, Shut-off if 3rd test above LAL[c]
Upper Action Level	≥25[b]	≥5[b]	Immediate Shut-off

a For any single constituent. Approach modified HI from 1993 ARB Guidance from 0.2 to 0.1.
b Sum of all constituents of concern exceeding trigger level. Approach modified upper action level from 1993 ARB Guidance from 100 chances/million and HI of 10, to 25 chances/ million and HI of 5.
c Within a 12 month period.

Proposed Cancer and Non-cancer Risk Management Levels

Constituent of Concern	Risk Management Levels (Health Based Standards) mg/m³ (ppmv)		
	Trigger Level	Lower Action Level	Upper Action Level
Carcinogenic Constituents of Concern			
Arsenic	0.019 (0.0062)	0.19 (0.062)	0.48 (0.15)
p-Dichlorobenzene	5.7 (0.95)	57 (9.5)	140 (24)
Ethylbenzene	26 (6.0)	260 (60)	650 (150)
n-Nitroso-di-n-propylamine	0.033 (0.0061)	0.33 (0.061)	0.81 (0.15)
Vinyl Chloride	0.84 (0.33)	8.4 (3.3)	21 (8.3)
Non-carcinogenic Constituents of Concern			
Antimony	0.60 (0.12)	6.0 (1.2)	30 (6.1)
Copper	0.060 (0.02)	0.60 (0.23)	3.0 (1.2)
Hydrogen Sulfide*	30 (22)	300 (216)	1,500 (1,080)
Lead	0.075 (0.0089)	0.75 (0.089)	3.8 (0.44)
Methacrolein	1.1 (0.37)	11 (3.7)	53 (18)
Alkyl Thiols	N/A (12)	N/A (120)	N/A (610)
Toluene	900 (240)	9,000 (2,400)	45,000 (12,000)

Monitoring Approach

- Monitor for constituents based on sources of biogas
  - 12 for landfill, 6 for POTW's, 5 for dairy
  - In general-annual monitoring for any CoC that is below trigger level, quarterly for any CoC above trigger level*

* H_2S to be monitored continuously if of concern

Constituent	Landfill	POTW	Dairy
Antimony	X		
Arsenic	X		
Copper	X		
p-Dichlorobenzene	X	X	
Ethylbenzene	X	X	X
Hydrogen Sulfide	X	X	X
Lead	X		
Methacrolein	X		
n-Nitroso-di-n-propylamine	X		X
Mercaptans (alkyl thiols)	X	X	X
Toluene	X	X	X
Vinyl Chloride	X	X	

Proposed Pre-injection Start-up Testing

- Conduct tests for the constituents of concern for biogas source
- Two pre-injection tests over 2-4 weeks
- Utility and biogas producer agree on an approach to monitor performance of biogas treatment system
  - Natural gas tariffs may be good surrogate for demonstrating biogas treatment system is functioning properly
- If all constituents of concern for that biogas source below LAL then can inject into pipeline

Repeat of Pre-injection Start-up Testing

- Repeat of pre-injection start-up testing to be conducted when:
  - There is a change in the biogas cleanup equipment design
  - A new source of biogas is accepted
  - Biomethane production process has been shut-off due to any exceedance of the UAL or more than 2 exceedances of the LAL in a 12 month period

Periodic Testing of Constituents of Concern

- Trigger level is applied to an individual constituent
- For individual CoC not detected or below the trigger level during pre-injection start-up
  - Require annual monitoring

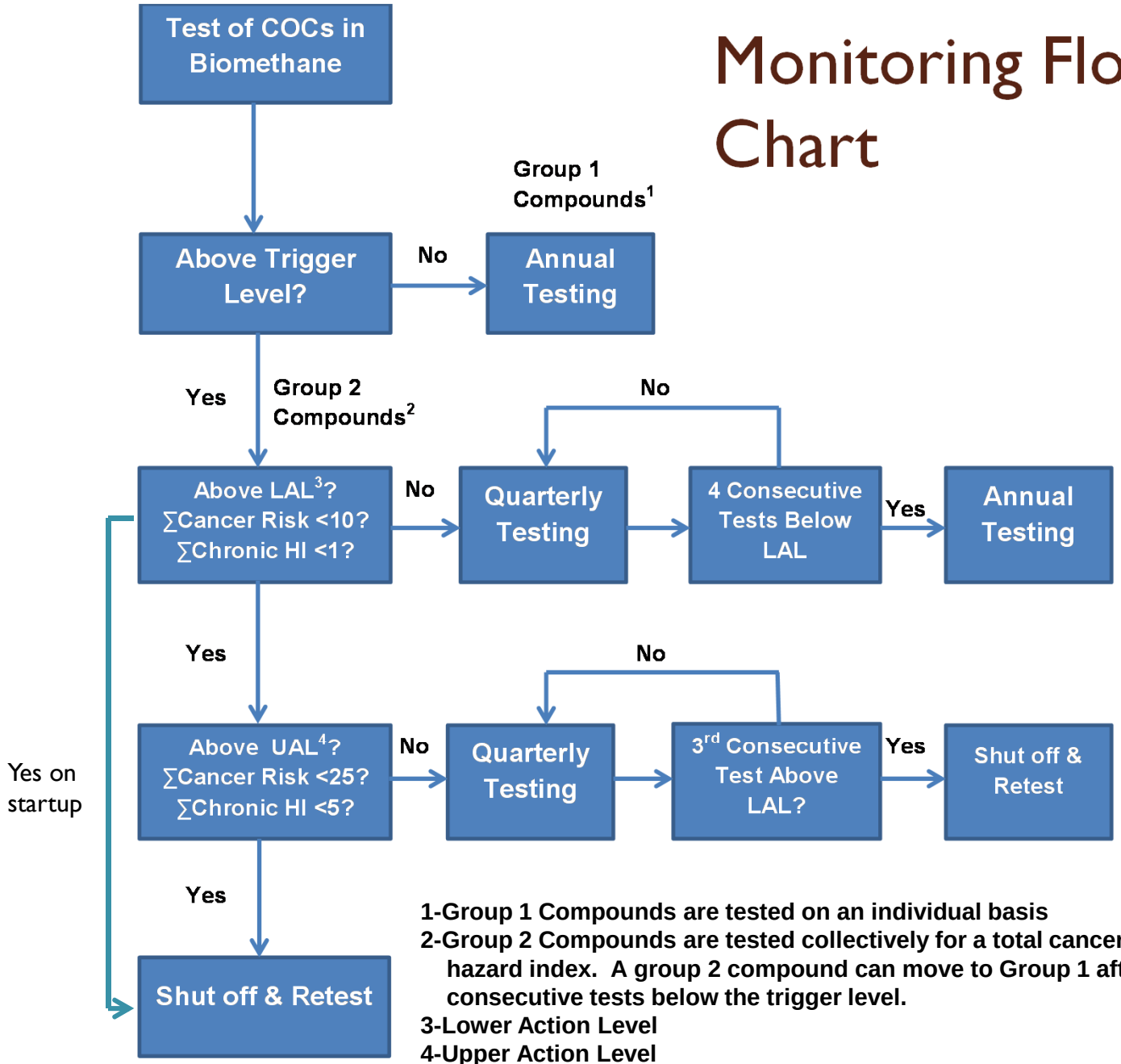
Periodic Testing of Constituents of Concern (cont)

- For CoCs above the trigger level require quarterly monitoring
  - For an individual CoC
    - If 4 quarterly tests in 12 month period demonstrate CoC below trigger level, then can go to annual testing
  - For the group of CoCs being monitored
    - LAL and UAL applied to combined risk for all CoCs monitored
    - Shut-off if total "combined" potential cancer and non-cancer risks exceed UAL, or if exceed LAL more than 2 times in 12 month period
    - If 4 quarterly tests in 12 month period demonstrate CoCs total risks below LAL then can go to annual testing
    - ARB to provide web-based tool to calculate total risks based on measured concentrations of CoCs

Example

- POTW biomethane producer wants to inject into the common carrier pipeline
- Tests 6 constituents of concern twice
  - 4 constituents individually below trigger level
  - 2 above trigger level but below LAL
- Biomethane producer and utility agree on approach to monitor performance of biogas treatment system
- Injection can start
  - Four constituents tested annually; other two quarterly

Monitoring Flow Chart



1-Group 1 Compounds are tested on an individual basis
2-Group 2 Compounds are tested collectively for a total cancer risk and hazard index. A group 2 compound can move to Group 1 after 4 consecutive tests below the trigger level.
3-Lower Action Level
4-Upper Action Level

Proposed Test Methods for CoCs

Proposed CoCs	Approximate Levels	Risk Type	Proposed Test Method
Metals	**ppb**		
Lead	9 ppb	Chronic HQ	EPA Method 29 (AAS and/or ICP)/ EPA 200.8
Antimony	120 ppb	Chronic HQ	EPA Method 29 (AAS and/or ICP)/ EPA 200.8
Arsenic	6 ppb	Cancer Risk	EPA Method 29 (AAS and/or ICP)/ EPA 200.8
Copper	23 ppb	Chronic HQ	EPA Method 29 (AAS and/or ICP)/ EPA 200.8
Nitroso Compds	**ppb**		
n-Nitroso-di-n-propylamine	6 ppb	Cancer Risk	EPA 8270 (GC/MS)
Sulfur Compds	**ppm**		
Hydrogen Sulfide	22 ppm	Chronic HQ	ASTM D4084 Lead Acetate Reaction Method
Total Mercaptans (alkyl thiols)	12 ppm	Chronic HQ	GTI used ASTM D6228
SVOCs	**ppm**		
Dichlorobenzenes (as p-Dichlorobenzene)	0.95 ppm	Cancer Risk	TO-15 (GC/MS)
VOCs	**ppb**		
Vinyl Chloride	330 ppb	Cancer Risk	TO-15 (GC/MS)
Methacrolein	380 ppb	Chronic HQ	TO-11 (Determination of Formaldehyde, Adsorbent Cartridge (HPLC))
Alkyl Benzenes	**ppm**		
Ethylbenzene	6 ppm	Cancer Risk	TO-15 (GC/MS)
Toluene	240 ppm	Chronic HQ	TO-15 (GC/MS)

Recordkeeping and Reporting Proposal

- Retain records of test results for 3 years
- Provide annual report to CPUC, ARB and OEHHA
  - All test data
  - Annual biomethane production rate
  - Monitoring parameters to ensure cleanup system operating effectively
  - Any shutdown event, reason and remedy
- If utility is testing entity, report to biomethane producer
  - Test results within 2 weeks, 24 hours for shutoff levels.
- If biomethane producer is testing entity, report to utility same information
- Other (?)

Open Discussion & Wrap-up

- Other discussion items
- Wrap-up and Summary
- Next Steps